Ozone uptake to the polar snowpack at Summit, Greenland

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Abstract

The uptake of atmospheric ozone to the polar, year-round snowpack on glacial ice was studied at Summit, Greenland during three experiments in 2003, 2004, and 2005. Ozone was measured at up to three depths in the snowpack, on the surface, and above the surface at three heights on a tower along with supporting meteorological parameters. Ozone in interstitial air decreased with depth, albeit ozone gradients showed a high variation depending on environmental conditions of solar radiation and wind speed. Under low irradiance levels, up to 90% of ozone was preserved up to 1 m depth in the snowpack. Ozone depletion rates increased significantly with the seasonal and diurnal cycle of solar irradiance, resulting in only 10% of ozone remaining in the snowpack following solar noon during summertime. Faster snowpack air exchange from wind pumping resulted in smaller above-surface-to-within snowpack ozone gradients. These data indicate that the uptake of ozone to polar snowpack is strongly dependent on solar irradiance and wind pumping. Ozone deposition fluxes to the polar snowpack are consequently expected to follow incoming solar radiation levels and to exhibit diurnal and seasonal cycles. The Summit observations are in stark contrast to recent findings in the seasonal, midlatitude snowpack [Bocquet, F., Helmig, D., Oltmans, S.J., 2007. Ozone in the mid-latitude snowpack at Niwot Ridge, Colorado. Arctic, Antarctic and Alpine Research, in press], where mostly light-independent ozone behavior was observed. These contrasting results imply different ozone chemistry and snowpack–atmosphere gas exchange in the snow-covered polar, glacial conditions compared to the temperate, mid-latitude environment.

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1. Introduction

The discovery of the drastic and complete removal of ozone in the air above the surface in coastal regions during the polar sunrise has motivated a plethora of subsequent research on cryospheric photochemical processes. This research has revealed the importance of photochemical radical chemistry, in particular of halogen reactions, in polar ozone chemistry (e.g. Barrie et al., 1988; Bottenheim et al., 1990; Barrie and Platt, 1997; Domine and Shepson, 2002). The sunrise ozone depletion events are episodic and constrained to the coastal, sea ice environment during the spring season (Helmig et al., 2007a). Other snow-photochemical processes have subsequently been discovered, and increasing evidence now suggests that...
a rather complex snowpack chemistry is driving a rigorous snowpack–atmosphere gas exchange that is of importance for the vast continental glacial ice sheets throughout the sunlit seasons (Dibb et al., 1998; Dibb and Arsenault, 2002; Sumner and Shepson, 1999; Hutterli et al., 1999, 2002; Jacobi et al., 2002, 2004; Swanson et al., 2002).

Field studies at Summit, Greenland, Antarctica and in Northern Michigan have demonstrated that interstitial air and surface layer levels of oxidized nitrogen species, including NO\(_x\) (NO\(_x\) = NO + NO\(_2\)) and HONO are greatly affected by snow-photodenitrification processes (Honrath et al., 1999, 2000a, 2002; Dibb et al., 2002; Jones et al., 1999, 2000, 2001; Beine et al., 2002; Davis et al., 2004). The mechanisms for production of nitrogen oxides (NO\(_x\)) have been further investigated in the laboratory (Honrath et al., 2000b; Cotter et al., 2003) yielding further evidence that these processes result from photolysis of trace levels of nitrate in the snow.

Tropospheric ozone is closely linked to chemical reactions involving oxidized nitrogen. Both ozone production and depletion chemistry are dependent on atmospheric levels of NO\(_x\), solar radiation and concentrations of hydrocarbons and radicals that drive the conversion rates in the NO \(\rightarrow\) NO\(_2\) and HO\(_x\) cycles. Several investigations have addressed the question of how active nitrogen oxide chemistry in the snowpack affects the loss or production of ozone in the snowpack and the overlying atmosphere.

During the summer 2000, Peterson and Honrath (2001) studied diurnal cycles of NO\(_x\) and ozone and their dependencies in interstitial air at \(-30\) cm depth in the polar snowpack at Summit. The snowpack measurements were compared with data from above the surface. Ozone and NO\(_x\) in firn air exhibited diurnal cycles with amplitudes of \(\sim10\) ppbv and \(\sim350\) pptv, respectively. These cycles were anti-correlated and directly determined by solar irradiance. While ozone in the snowpack was lowest during the time of maximum solar radiation (noon), mixing ratios of NO\(_x\) were highest. These measurements suggest that ozone destruction is linked to photodenitrification processes in the snowpack.

Photochemical ozone chemistry was also investigated at Alert, Canada, in the context of polar sunrise ozone depletion events (Albert et al., 2002). Ozone was measured at up to nine depths in the interstitial air of the \(~50\) cm thick snowpack during the dark, twilight and summertime light conditions. During all times, ozone concentrations in the snowpack declined significantly with depth. Ozone gradients were \(\sim0.5–2\) ppbv cm\(^{-1}\). At \(50\) cm depth, remaining ozone was \(<10\%\) of ambient air concentrations. Kinetic chamber experiments showed that ozone loss in sunlit snow was approximately three times higher than the loss rate during a dark experiment. Albert et al. (2002) presented several hypotheses for a possible ozone destruction mechanism, including catalytic removal by black carbon, and reaction with humic and fulvic acids. These experiments imply that, similar to Summit, ozone destruction in snow at Alert has a photochemical contribution. The snowpack gradient data from the dark period also indicated that at Alert a significant fraction of ozone destruction stems from a dark reaction mechanism.

The role and influence of snowpack ozone chemistry on the fluxes between the atmosphere and the snowpack is of interest for considerations of the tropospheric ozone budget and possible feedbacks of snowpack contaminants as well as snow cover changes on tropospheric ozone. Tropospheric ozone levels at high northern latitudes during winter strongly depend on ozone surface deposition. A recent review (Helmig et al., 2007b) pointed out the large range of previously measured ozone deposition velocities to snow. Interestingly, several studies have found positive, upward ozone fluxes over snow-covered alpine landscapes (Galbally and Allison, 1972; Zeller and Hehn, 1994, 1996; Zeller, 2000). It is plausible that the high discrepancy in the published ozone flux data is due to spatially and temporally highly variable ozone photochemistry in the snowpack, which may be a determining factor for ozone atmosphere–snow fluxes.

In this paper we report snowpack experiments performed during three campaigns at Summit. These investigations are contrasted with similar experiments that were recently performed in the temperate snowpack in the Colorado Rocky Mountains and which were reported by Bocquet et al. (2007). The goal of this research was to investigate sinks (and possible sources) of ozone at the snowpack–atmosphere interface and the processes that determine the ozone atmosphere–snowpack gas exchange. Concurrent ozone flux measurements during the three campaigns at Summit will be presented in a later publication.

2. Experimental methods

The Greenland Environmental Observatory at Summit (GEOSummit) is located at 72.34°N,
38.29°W, 3212 m above sea level near the center of the Greenland ice cap. Experiments were performed during 19 July–30 July 2003, 22 March–14 August 2004, and 17 March–28 April 2005. All measurements were done at the ‘Science Trench’ (Fig. 1). The Science Trench tower was equipped with instruments for measurements of wind speed gradients (cup anemometers, Model 010C, Met One Instruments, INC, Grants Pass, OR) at 0.5, 2, and 10 m, temperature gradients (aspirated E-type thermocouples with radiation shield, Model 43408, R. M. Young Company, Traverse City, MI) at 0.5, 2, and 10 m, wind speed and wind direction at 2 m (Model 034B, Met One Instruments), snow surface temperature (Model 4000.4ZL, Everest Interscience INC, Tuscon, AZ) and snow accumulation (ultrasonic distance sensor, Model SR50, Campbell Scientific Instruments, Logan, UT). Incoming and reflected solar radiation (LI200X pyranometers, Campbell) were measured ~3 m south of the tower on a pole, at 1.35 m height above the surface. After the Summit experiments we found out that extension cables used for the pyranometers caused an attenuation of measured radiation data. The radiation data were later compared with other measurements and our data from these measurements were found to be ~7% lower than actual conditions. Snowpack temperature was measured with a type E thermocouple wire. The ~1 m towards the end of the thermocouple wire was covered with white heat shrink tubing to reduce radiation artifacts. Shown measurement heights were for the 2003 experiment; later experiments were conducted in a similar fashion, measurement heights and depths changed during extended experiments (2004, 2005) due to snow accumulation.

Air was drawn from the snowpack through 18 m long, 6.4 mm o.d., 4.0 mm i.d. PFA sampling lines (perfluoralkoxy-polymer (PFA) tubing). In order to avoid sampling of ice and snow particles, two different types of inlet designs were used. During 2003, inlet line ends were capped with plastic caps and a series of ~fifty 0.16 mm diameter holes were drilled into the 5 cm of the tubing next to the cap. During later experiments, glass fiber syringe filters (Acrodisc, 1 µm pore size, product number 4523, VWR International, San Dimas, CA) were used. All tubing and inlet filters were conditioned prior to the experiment by sampling of ~250 ppbv of ozone for at least 24 h. Inlets were installed into the snowpack by excavating a ~30 x 30 cm snow pit from which a horizontal, ~30 cm bore hole was made in which the Teflon line inlet was inserted. Subsequently, the bore hole and snow pit were backfilled and tightly compressed with clean snow. Ozone from the tower inlets was sampled through PFA inlet funnels with PTFE (polytetrafluoroethylene) membrane (Savillex Corp., Minnetonka, MN) filters and three individual ozone analyzers sampled air continuously from these inlets. The snowpack sampling was done by continuously pulling air from ~30 cm depth during 2003. During 2004, a sampling manifold was used and air was sampled intermittently from each of the 3 inlets in 10 min-intervals. The manifold and components were similar to the ones described in detail by Bocquet et al. (2007). During 2004, an additional sampling inlet (with inlet filter) was placed right on the snow surface. This inlet typically got covered by precipitating or blowing snow within a few hours to a day. The inlet was cleared of snow and repositioned on the surface as soon as we noticed that it was submerged. All meteorological data and analog outputs from the ozone monitors were recorded with a data logger (Model 23 X, Campbell Scientific).

UV photometric TEI Model 49C analyzers (Thermo Electron Corporation, Franklin, MA) were used. A TEI Model 49, a Dasibi Model 1003-AH (Dasibi Environmental Corporation, Glendale, CA), and a 2B Monitor (2B Technologies, INC, Golden, CO) were used for the snowpack ozone sampling. All instruments were calibrated against a laboratory standard monitor (which was referenced against the National Institute for Standards and Technology, Gaithersburg, Maryland ozone Standard Reference Photometer) prior to field deployment. The Model 49C monitors were found to yield an accuracy and precision of ~1 and 0.1 ppbv, respectively for 1-min data. All other analyzers had accuracies in the range of 1–2 ppbv and a precision in the range of 0.5–1.5 ppbv. Air flow through the sampling lines, which was in the range of ~0.6–1.41 min⁻¹, was delivered by the sampling pumps of these monitors. The firn air sampling lines had union connectors near the tower base. The lines were opened for 30-min periods every week and run in parallel with the 2 m-tower inlet in order to intercompare the firn air ozone monitor with the higher precision tower gradient monitors. Agreement between these two measurements varied but typically was better than ~±2 ppbv. The firn air data were not corrected for this small and variable measurement bias. Firn air was pulled sequentially for 10 min through each of the 3 inlets, 1 min each, to equilibrate the inlets with the snowpack.

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the three sampling lines during 2004. This cycle resulted in $2 \times 10$ min air sampling at each depth per hour and an effective air volume of $\sim 2 \times 151$ that was collected from each inlet depth per hour. Bocquet et al. (2007) showed that this intermittent sampling approach yielded excellent agreement with observations from continuously sampling instruments. Ozone monitors and the data logger were
inside a temperature-controlled (~20 °C) container that was located in the underground laboratory of the Science Trench.

The firn air sampling increases the natural gas transport through the snowpack, which is driven by wind pumping, advection, thermal convection and diffusion processes. Furthermore, snow physical properties, e.g. size and distribution of snow grains, affect the airflow in the snowpack (Albert et al., 2002; Albert and Shultz, 2002). Air flow and gas transfer through the snowpack can vary widely depending on these conditions. Wind pumping becomes the dominant transport mechanism at higher wind speeds. Wind ventilation in the upper 10 cm of snowpack at moderate winds (7–9 m s\(^{-1}\)) was found to be more than an order of magnitude larger than molecular diffusion rates in snow (Albert et al., 2002). These studies also showed that interstitial air, which is collected by continuous pulling of air through the snowpack, will have a large contribution from air that is directly pulled from the surface through the snowpack above the inlet. The contribution of this bias will become smaller with increasing wind speeds. Ideally, measurements should be made in small volumes drawn from the snowpack. Our snowpack sampling flow rate (~1 min\(^{-1}\)) is relatively low compared to other snowpack studies. For example, ~21 min\(^{-1}\) were sampled for the ozone measurements by Albert et al., (2002), and 21min\(^{-1}\) for the NO\(_x\)/O\(_3\) experiments by Peterson and Honrath (2001). Secondly, the intermittent air sampling that was used during 2004 further reduced the integrated volume-over-time sampling (and induced snowpack ventilation), as air was only sampled during ~1/4 of the time from each inlet. The comparison of data from the continuous sampling (2003) with the intermittent sampling (2004) does not show any qualitative differences. From these experiments and further experiments detailed elsewhere (Bocquet et al., 2007) we conclude that the snowpack sampling was not the dominant air ventilation process, but that natural gas transfer provided most of the snowpack ventilation and that observed ozone gradients are indicative of actual chemical gradients in the undisturbed snowpack.

3. Results and discussion

Measurements of ozone at the surface, in interstitial air and of ozone fluxes were performed during a total of 194 days in 2003, 2004 and 2005. The experiments conducted during the later two campaigns were somewhat modified and expanded, incorporating experiences from the earlier observations. The basic findings from the three experiments were in full agreement and this paper presents excerpts from these different data sets to illustrate the most important results.

A week of ozone measurements at three snowpack depths and from above the surface during April 2004 is shown in Fig. 2(a). The sampling depths increased due to snow accumulation during the 2004 experiment. Adjusted sampling depths, which were calculated from the initial inlet installation depth and the snow surface height are used throughout the data discussion. Effective inlet depths for the experiment in Fig. 2(a) were ~−40, −70 and −90 cm. It is striking that ozone levels in the snowpack are similar and not much lower than above the snow surface. Ozone trends in the snowpack follow ambient ozone. The ozone gradients between the three inlets are small, e.g. ozone at −90 cm depth is not much lower than at −40 cm. These data infer that ozone is well preserved in the snowpack, likely to depths much deeper than probed with our experiment. Superimposed on the day-to-day changes in ozone, a diurnal cycle in the snowpack ozone is evident. This diurnal cycle is anti-correlated with the solar irradiance cycle, which is also included in this figure. Snowpack ozone declines during the day, typically dropping ~5–15 ppbv below ambient air levels. The magnitude of this signal is somewhat variable. During night, ozone in the snowpack re-equilibrates with ambient air concentrations. Even at −90 cm, snowpack ozone typically was within ~1–5 ppbv of ambient air ozone during night. The firn air ozone minima were reached ~1–2 h after the time of solar maximum. During this period in early April, daytime maximum radiation peaked around 500 W m\(^{-2}\). During the night, solar irradiance dropped below 1 W m\(^{-2}\) for ~7 h. The 24-hour mean, incoming solar radiation during this one week period was 177 W m\(^{-2}\).

The April data are contrasted with results from July (Fig. 2(b)). Due to the snow accumulation between April and July, the inferred sampling depths during the later periods are deeper (i.e. −50, −80 and −100 cm). Noontime, maximum incoming radiation levels during this period were ~700 W m\(^{-2}\). At Summit, which is north of the Arctic circle, the sun does not set below the horizon during the summer; nighttime solar irradiance levels
drop to \( \sim 50 \text{ W m}^{-2} \). The 24-hour, mean incoming radiation was 353 W m\(^{-2} \), approximately two times the integrated irradiance during April. Under these conditions, ozone in the firn air exhibits a stronger depletion and observed diurnal cycles show a higher amplitude than during April. Firn air ozone minima are still observed a few hours after solar noon, but with only 10–50% of ambient ozone remaining in the snowpack during the afternoon. During nighttime, even though solar radiation remains above \( \sim 50 \text{ W m}^{-2} \), ozone in the snowpack recovers significantly. Nighttime maxima remain \( \sim 10 \text{ ppbv} \) below ambient air ozone mixing ratios, though on several days (day of year (DOY) 181, 182 in Fig. 2(b)), when ambient ozone dropped by more than 10 ppbv within a few hours, ozone levels in the snowpack were close, and for several hours on DOY 182, even higher than above the surface. The
comparison of these ozone time series illustrates a 2–3 h delay between the ambient and snowpack ozone, which reflects the transport and equilibrium time of ambient ozone with the snowpack air (see more discussion below). Ozone gradients during these two periods are further analyzed in Fig. 3. Data were binned into 4-hour intervals and the mean diurnal ozone (with standard deviation) was plotted against the sampling depth. This comparison further illustrates both the much higher depletion rate during the daytime hours and the higher losses of ozone in the snowpack during the June/July period.

For DOY 200–211, 2003 data were binned in 30-min intervals and the deviation from the diurnal mean ozone above the snowpack and at −30 cm with their standard deviation were calculated (Fig. 4). The median ozone mixing ratios for ambient and firn air during this period were 47.4 and 35.3 ppbv, respectively. No significant diurnal cycle is seen in the ambient ozone data. The diurnal ozone cycle in the snowpack shows a ~12 ppbv amplitude. The GMT times of solar minimum (2:34) and maximum (14:34) were calculated from the site longitude and added to this figure as vertical lines. Diurnal ozone maxima and minima in the interstitial air occur ~2 and ~3 h after solar minimum and maximum, respectively.

Given the weakness of the diurnal ozone cycle in ambient air (Fig. 4), ozone gradients between ambient air and interstitial snowpack air follow a diurnal cycle with highest gradients occurring during the sunlit hours. Since gas fluxes in the atmosphere are driven by concentration gradients, ozone fluxes into the snow are expected to be largest during the day. This stronger ozone sink during the sunlit hours would be expected to result in a parallel decline of ambient ozone. Such a decline obviously is not seen in the ambient air data. Yang et al. (2002) estimated a net photochemical ozone production rate of 2–3 ppbv day$^{-1}$ at Summit for the conditions encountered during summer 1999 and 2000. Diurnally increasing ozone in the surface layer would be expected from this ozone production. Neither the data in Fig. 4 nor other analysis of diurnal ozone cycles at Summit (Helmig et al., 2002, 2007a) reflect this expected ozone production. Therefore, it appears possible that both the diurnal ozone production and diurnal ozone deposition fluxes are of similar magnitude and offset each other. A more conclusive interpretation of these observations is anticipated from our ongoing analysis of ozone surface flux data.

The approximate times of all diurnal minima and maxima were determined for each inlet depth for the 127-day period of the 2004 experiment. These data were then plotted against the year 2004 DOY (Fig. 5). Because of the weaker diurnal signal during the early spring period, the determination of the times of minimum and maximum was more

Fig. 3. (a), (b) Ozone in the snowpack and at the surface for 7 days during the periods shown in Fig. 2 was binned into 4-hour intervals and the mean values at a given sampling depth were plotted against the inlet depth. Ambient ozone from the tower (at 0.5 m) was used to represent the surface ozone mixing ratio (ozone gradients between the surface and the 0.5 m inlet generally were much smaller than the snowpack gradients). X-axis error bars are the mean standard deviation at each depth for the 4-hour measurement interval. Y-axis error bars are estimated uncertainties in the sampling depths.

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uncertain, which is reflected by the larger scatter of earlier data points in Fig. 5. Regression lines were calculated through the six data series and are included in the figure. The regression lines re-emphasize observations from Fig. 2, e.g. both minima and maxima are observed at later times with increasing sampling depth. This delay reflects the transport of the ozone-depleted air (respectively at night, the depleted snowpack air is replenished by higher concentrations of ozone in ambient air) deeper into the snowpack. The mean time shifts of the minima and maxima at the next deeper inlets (calculated from the regression line functions for the last day of the experiment, DOY 226) were used to estimate the mean transport time and velocity of the ozone signal in the snowpack. This calculation yielded a value of 0.55 cm min\(^{-1}\) for the distance between the \(-30\) cm to the \(-80\) cm inlets and 0.42 cm min\(^{-1}\) for the \(-80\) cm to the \(-100\) cm inlet (given inlet depths are for the end of the experiment).

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An interesting feature in this plot (Fig. 5) is the fact that all regression lines are sloped upwards, indicating later times for the minima and maxima as the season progressed. This behavior is not surprising as the inlets were kept in place during this whole period and the effective measurement depths increased with snow accumulation during the duration of this experiment. The mean slope of the six regression lines is $3.3 \pm 1.8 \times 10^{-3} \text{d DOY}^{-1}$, equivalent to 0.29 min d$^{-1}$ (62 min total shift during the entire 2004 study). The measured increase in the sampling depth during this time, was $\sim 40 \text{cm}$. From these two measurements we infer an average, effective transport time between the surface and the three sampling inlets of 0.65 cm min$^{-1}$. This estimate, based on the snow accumulation rate, compares reasonably well with the aforementioned calculation, which used the time shifts of the diurnal minima and maxima at different depths.

From Fig. 3 it is clear that most of the ambient ozone is destroyed between the surface and the first snowpack sampling inlet. Comparatively small differences, indicating less ozone loss, are seen deeper in the snowpack. The question whether ozone was mostly destroyed at the surface–atmosphere interface or in the snowpack, within the first 30 cm below the surface, was investigated by sampling air from an inlet that laid right on the snow surface. The data from these measurements can be compared to ozone measurements at 2 m on the tower in Fig. 2(a). The surface measurements show some deviations from the ambient air data, however most of these differences can be explained by the lower precision and accuracy of the ozone monitor that was used to measure ozone at the snow surface, and by the fact that the inlet was intermittently covered by a dusting of blown snow. Except of these slight deviations, the surface ozone resembles ambient air concentrations and lacks the diurnal destruction cycle within the snowpack. Secondly, ozone gradients between the tower inlets and the surface inlet are small. Taken together, these two features illustrate that ozone is destroyed within the snowpack and not at the surface. Photochemistry is expected to maximize in the near-surface layer and to decline with increasing depth, according to the light attenuation in the snowpack. Both radiation and nitrate photolysis measurements showed that e-folding depths for solar radiation and photolysis frequencies (NO$_2$, NO$_3$, H$_2$O$_2$) are in the $\sim 5$–20 cm range (Peterson et al., 2002; Qiu et al., 2002; Philips and Simpson, 2005; Galbavy et al., 2007a, b). Ninety percent of photo-oxidation of OH was found to occur in the top 10 cm of the snowpack (Anastasio et al., 2007). These similarities in the depth dependencies of the penetration of radiation, photolysis rates, radical formation and ozone profiles further suggest that ozone chemistry is linked to these photochemical processes and that most photochemical activity occurs within the upper centimeters of the snowpack.

Even though the data series in Figs. 2(a) and (b) show a regular diurnal cycle of ozone in firn air, the amplitude of the ozone destruction appears to have some day-to-day variations. We further investigated the influence of snowpack ventilation processes on the ozone gradient. Snowpack ventilation is driven by several contributing processes including wind pumping, the induced air flow from the sampling procedure, thermal convection, and gas diffusion.

Temperature gradients between ambient air and the firn air change during day and night. This behavior causes the potential for thermal convection and possibly increased mixing. This effect was investigated by comparing temperature measurements of firn air (at $\sim 30 \text{cm}$), of the snow surface temperature, and of ambient air temperature at $+30 \text{cm}$ (Fig. 6). These three temperature time series illustrate the rather strong changes in temperature gradients in the upper 30 cm of the snowpack. At $\sim 30 \text{cm}$, snowpack temperature changes much less than at or above the surface. A 1–2°C warming is typically observed during the day. Firn air temperature follows ambient air temperature trends, but with a much attenuated signal, and with a 6–12 h lag in the diurnal cycle and a several days delay in the temperature changes that occur over 2–4 days. The snow surface temperature is driven by the daytime solar heating and nighttime radiative cooling cycle. The amplitude of this diurnal cycle varies from 5 to 20°C, with most of the variation stemming from variable cooling during the night, which will be higher during clear nights and lower during nights with low and heavy cloud cover. Ambient air temperatures near the surface follow closely the surface temperature, though daytime maxima are $\sim 1$–4°C lower and nighttime minima are $\sim 1$–2°C higher than the surface temperature. The important point is that the sign of the temperature gradient between firn air and the surface changes between day and night. During nighttime, the radiative cooling of the surface snow results in up to $\sim 25$°C warmer temperatures in the snowpack (at $\sim 30 \text{cm}$). This
A large thermal gradient is expected to result in thermal convection (Powers et al., 1985), and consequently faster gas exchange within the snowpack, and between the snowpack and the atmosphere. This increase in convection would be expected to cause faster mixing and to possibly contribute to higher ozone mixing ratios in the snowpack during night.

The dependency of the ozone gradient (ambient–snowpack) on the snowpack temperature gradient as well as on wind speed (at 10 m) is shown in Fig. 7. High ozone gradients are indicative of much lower (than ambient) ozone levels in the snowpack. Low (negative) temperature gradients (mostly present at night) are indicative of warmer temperatures in the snowpack (and potentially larger mixing from thermal convection). These comparisons show that high ozone gradients (>25 ppbv) are correlated with lower wind speeds (e.g. DOY 201, 205). Low ozone gradients are correlated with higher wind speed conditions (e.g. DOY 207, 208). Negative snowpack temperature gradients typically are followed (within a few hours) by low ozone gradients (high ozone concentrations in the snowpack). But it is difficult to discern if the correlation between the temperature gradients and ozone gradients is from a lower nighttime destruction rate or from the faster replenishing of snowpack air with air from above the surface. Notably, neither of the two situations with the lowest temperature gradients (DOY 207 and 211) coincide with the smallest ozone gradients. However, during all three occasions with ozone gradients <3 ppbv (DOY 201, 208, 209), winds either shortly before had been or at the same time were above average. These comparisons suggest that snowpack ventilation from wind pumping is a more obvious cause of the snowpack ventilation than thermal convection.

The influence of wind-driven ventilation is further investigated in Fig. 8, where the ambient-firn air ozone gradients were binned into two 12-hour groups for the times of maximum and minimum solar radiation and plotted against wind speed (at 2 m) for the July 2003 experiment. Both data series show the dependency of the ozone gradient on wind pumping. In both data sets, ozone gradients decline with increasing wind speed. These dependencies are further illustrated by linear regression lines that were fit through both data series. Ozone gradients during the higher solar radiation conditions are ~2 times larger than during the low radiation conditions. In both groups of data, ozone gradients decline to about half at wind speeds of ~7–8 m s⁻¹ and to about one third at ~11 m s⁻¹.

From these aforementioned analyses it is apparent that ozone gradients are predominantly determined by solar irradiance and the rate of snowpack ventilation by wind pumping. The overall dependency on both of these variables are illustrated in Fig. 9 where ozone gradient data for the 2003 experiment were averaged and interpolated in a color contour plot against both radiation and wind speed. This graph confirms the earlier conclusion and shows the determining influences of both radiation and wind pumping on the ozone depletion.
in the snowpack. The largest gradients (>20 ppbv) are observed at conditions of >500 W m\(^{-2}\) and <4 m s\(^{-1}\) whereas small gradients (<5 ppbv) are observed when radiation drops to <100 W m\(^{-2}\) and at wind speeds >8 m s\(^{-1}\).

It should be noted that other processes (that were not further investigated by our experiments) may effect the ozone concentration in the snowpack. For instance, it has been suggested that ozone may be taken up by snow crystals or the quasi-liquid layer and be subsequently released (degassing) when temperatures increase (Galbally and Allison, 1972; Zeller and Hehn, 1996; Zeller, 2000). As significant diurnal temperature changes only occur in the

![Fig. 7. Ozone gradient (black data points, ozone at +30 cm minus ozone at −30 cm), wind speed at 10 m (dark gray), and temperature gradient (temperature at the surface minus temperature at −30 cm, light gray) during July 2003.](image)

![Fig. 8. Ozone gradient (ozone mixing ratio at 2 m above the surface minus ozone mixing ratio at −30 cm) during DOY 200-212, 2003 as a function of wind speed. The data were grouped into the 12-h periods of maximum solar radiation (9:15–21:15 GMT, open squares) and the period of minimum solar radiation (21:15–9:15 GMT, crosses) during this period.](image)
uppermost layers of the snowpack, such effects would be expected to be most important in the proximity of the snow surface. Flow of dry air through the snowpack causes thermal effects (from sublimation, heat conductance) and mass transfer (due to sublimation and water vapor freezeout) (Albert and McGilvary, 1992), which further complicates the differentiation between the influences of photo-chemistry, quasi-liquid layer processes, thermal effects and transport phenomena on the observed ozone profiles in the snowpack.

During all three Summit experiments, interstitial air ozone generally was less than (or, in a few occasions just about equal to) ozone in ambient air. A very few exemptions were observed during periods when rapid declines in ambient ozone occurred. In those incidents (e.g. DOY 103, 105, 182 (Fig. 2(b))), the delayed decline in firn air ozone caused conditions (lasting no more than 1–2 h) where ozone in the firn air was slightly (∼1–3 ppbv) higher than ambient air levels. Since gas fluxes in the environment occur from high to low concentrations, under such conditions, the possibility of an upward ozone flux exist. This effect is further investigated in Fig. 10, where the ozone gradients observed on the tower (ozone at 10 m minus ozone at 0.5 m) are plotted against the change of the ambient air ozone mixing ratio that was measured during the same hour. Plotted data points are 5-min averages for the 19 March–27 April 2004 period. Positive ozone gradients (lower ozone near the surface) are indicative of ozone uptake to the snowpack; negative ozone gradients are indicative of higher ozone right above the snow surface, a condition that will cause upward ozone fluxes. Positive ozone change values indicate increasing ambient surface ozone, whereas negative ozone change values indicate declining ambient surface ozone. It is clear that far more frequently conditions with positive ozone gradients (implying ozone deposition to the snowpack), as well as overall higher positive ozone gradients than negative ozone gradients are observed. Large positive ozone gradients were mostly measured during very stable surface layer conditions, when ozone loss to the surface is faster than replenishing through vertical air transport. In order to allow a quantitative comparison of the abundance of these different conditions, for each quadrant the sum of the product of the x- and y-value for each data point was calculated (resulting $\Sigma$-values are given in each quadrant of the figure). As a first approximation, it can be assumed that ozone fluxes will depend on the size of the gradient. The ratio of the $\Sigma$ of positive gradients (1570 ppbv$^2$ h$^{-1}$) to the $\Sigma$ of negative gradients (190) is ∼8:1, which indicates that conditions for ozone
deposition occur 8 times more frequent (resp. are stronger) than for upward ozone fluxes. For conditions when ambient air ozone decreases, the calculated $\Sigma$ value (125) is $\sim$two times higher than for conditions with increasing ambient ozone. This comparison illustrates that occasionally conditions of upward ozone fluxes existed, although far less frequently than for downward fluxes. These situations occurred with relatively (~2 times) higher frequency when ambient ozone levels declined, which caused ozone in the snowpack to be temporarily higher than in ambient air.

These findings conclusively show that downward ozone fluxes are the expected predominant condition at Summit. The firn air measurements imply that ozone fluxes will be strongly linked to solar radiation and winds. Both radiation and wind speed show seasonal variation at Summit. The strong cycle of irradiance is expected to be the determining factor for surface ozone fluxes. Winds generally are stronger and longer periods with sustained high winds are observed during the winter (Albert and Hawley, 2000), which suggests a possibly stronger wind-driven contribution towards ozone deposition during the winter. However, since the depletion of ozone in the snowpack during the dark winter months is much reduced compared to the summer, the contribution of stronger winds during winter is likely to be of minor importance. Also, the top layers of the snowpack at Summit are less permeable during the winter months; overall the snowpack ventilation remains at similar levels yearround.

Conditions at Summit are in contrast to findings from two other locations. At Alert, ozone in the snowpack appeared to be depleted not only during daylight, but also during the dark. Albert et al. (2002) concluded that “photochemistry may play a role in ozone destruction within the snowpack after sunrise, but a dark destruction mechanism must also exist to explain the data obtained during the dark period ...”. The snowpack studies at Niwot Ridge have similarly revealed a significantly different ozone behavior occurring in this seasonal snowpack. An obvious different condition at Summit is that the snowpack lies on top of an inert, gas-impermeable glacial ice sheet. As further detailed by Bocquet et al. (2007), these comparisons suggest that ozone chemistry in the seasonal snowpack is influenced by soil biochemistry, snow-pack stratigraphy, and the highly variable magnitude of the gas transport between the soil and the atmosphere through the permeable snowpack.

Several mechanisms for ozone destruction in the sunlit snowpack, possibly involving heterogeneous processes, have been proposed. These include halogen (e.g. bromine) chemistry (Peterson and Honrath, 2001), and reactions with traces of crustal materials, black carbon, or possibly humic and fulvic acids in the snowpack (Albert et al., 2002). Several new observations have since become available to further elucidate these questions. Hydroxyl
variable hydroxyl radical mixing ratios, peaking at C2-C6 alkenes and dienes range from 5 compounds. Ozone reaction rate constants with ozone reacts readily with unsaturated organic radicals (OH) are formed in the upper layers of the snowpack at rates of 130–610 nmol$^{-1}$ h$^{-1}$, with most of the OH stemming from photolysis of H$_2$O$_2$ (Anastasio et al., 2007). Indirect measurements of OH radical concentrations in the Summit snowpack (Beyersdorf et al., 2007) showed diurnal and variable hydroxyl radical mixing ratios, peaking at $3.2 \times 10^8$ molecules cm$^{-3}$. OH reacts with ozone at $k = 4.4 \times 10^{-14}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ (at 258 K) (Atkinson et al., 2004), which is much too slow to cause any appreciable loss of ozone at the stated OH mixing ratio. It is well established that ozone reacts readily with unsaturated organic compounds. Ozone reaction rate constants with C2-C6 alkenes and dienes range from $5 \times 10^{-20}$ to $1 \times 10^{-17}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ (Atkinson, 1994). Firn profile measurements of organic trace gases have indeed shown a significant enhancement of photochemically formed alkenes in the firn air. Ethene, propene and 1-butene had distinct maxima in the ~0 to ~50 cm firn layer and daytime mixing ratios were ~170 pptv, ~100 and ~50 pptv, respectively (Swanson et al., 2002). At such levels these three potential reactants would consume ~10% of the present ozone within four hours, which could account for a portion, but not all of the observed ozone loss. Other alkenes were not reported in these canister measurements and it is uncertain if this analysis did cover the full range of potential unsaturated hydrocarbons in the snow. Other unsaturated (e.g. biogenic) organics are known to exhibit much faster reaction with ozone (e.g. at up to $1 \times 10^{-14}$ cm$^3$ molecules$^{-1}$ s$^{-1}$). It appears possible, that other photochemically generated, yet unidentified, unsaturated organic trace gases may make a further contribution to the observed ozone destruction rate.

4. Conclusions

The diurnal and seasonal dependencies of ozone cycles indicate that photochemical destruction is the dominant ozone loss mechanism in the Summit snowpack. Most of the ozone is destroyed within the upper layers (30 cm) of the snowpack. In the absence of sun light, ozone is conserved in interstitial air to depths of at least ~1 m, likely to even deeper levels, and does not undergo any apparent loss reactions. These measurements provide evidence that ozone gas exchange between the polar snowpack and the surface layer can be bi-directional, though upward fluxes out of the snowpack only occur during rare occasions. This latter condition is observed when fast concentration decreases in the surface layer drive upward, re-equilibration fluxes during conditions with temporarily higher ozone in the snowpack than in the air above. This phenomenon was not observed in the midlatitude snowpack at Niwot Ridge.

Since ozone chemistry is closely linked to reactions involving other important oxidants and trace gases, the dependencies described in this work will probably be of similar importance for sources and sinks of other reactive gases that follow photochemically driven formation/destruction cycles.

The destruction of ozone in the snowpack on the Greenland glacial ice sheet shows much different dependencies than in seasonal snow with subniveal (under the snowpack) soil. We hypothesize that ozone deposition fluxes will show diurnal and seasonal variations in the polar regions and consequently will differ significantly between polar and midlatitude environments. These snowpack measurements suggest that probably ozone deposition to polar snowpack during the dark winter months becomes very small, which is in agreement with a recent sensitivity study of ozone chemistry during the Arctic winter (Helmig et al., 2007b).

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